

Poly(4,4-di(2-ethylhexyl)-cyclopenta[2,1-*b*:3,4-*b'*]-dithiophene-*alt*-2,1,3-benzothiadiazole) (PCPDTBT)-type copolymers synthesized by Direct Arylation Polycondensation

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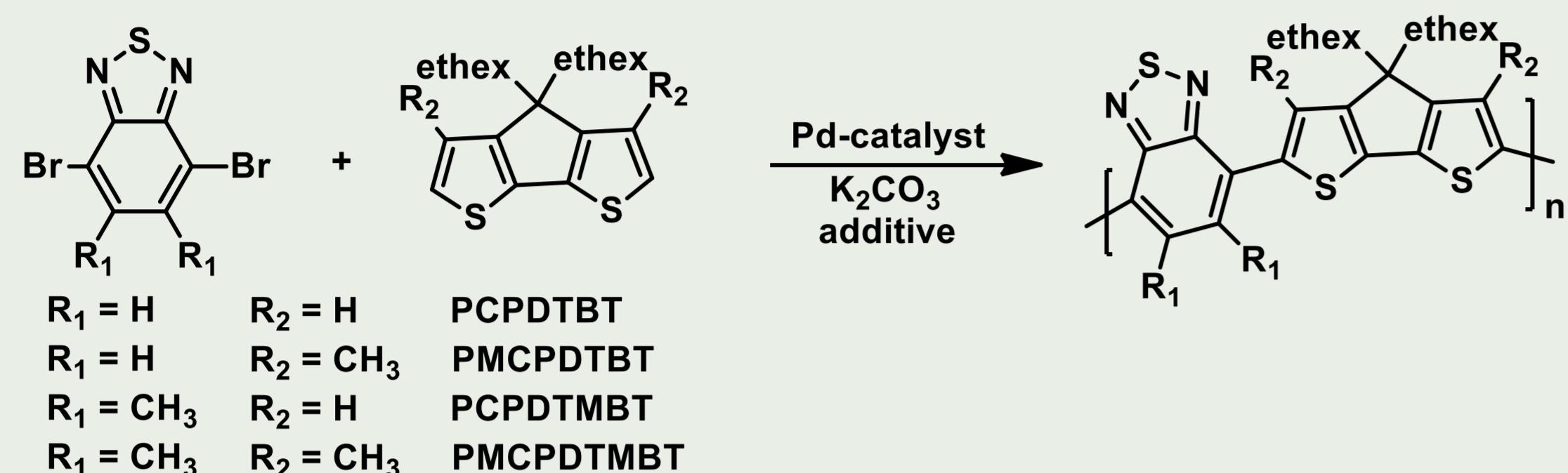
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Introduction:

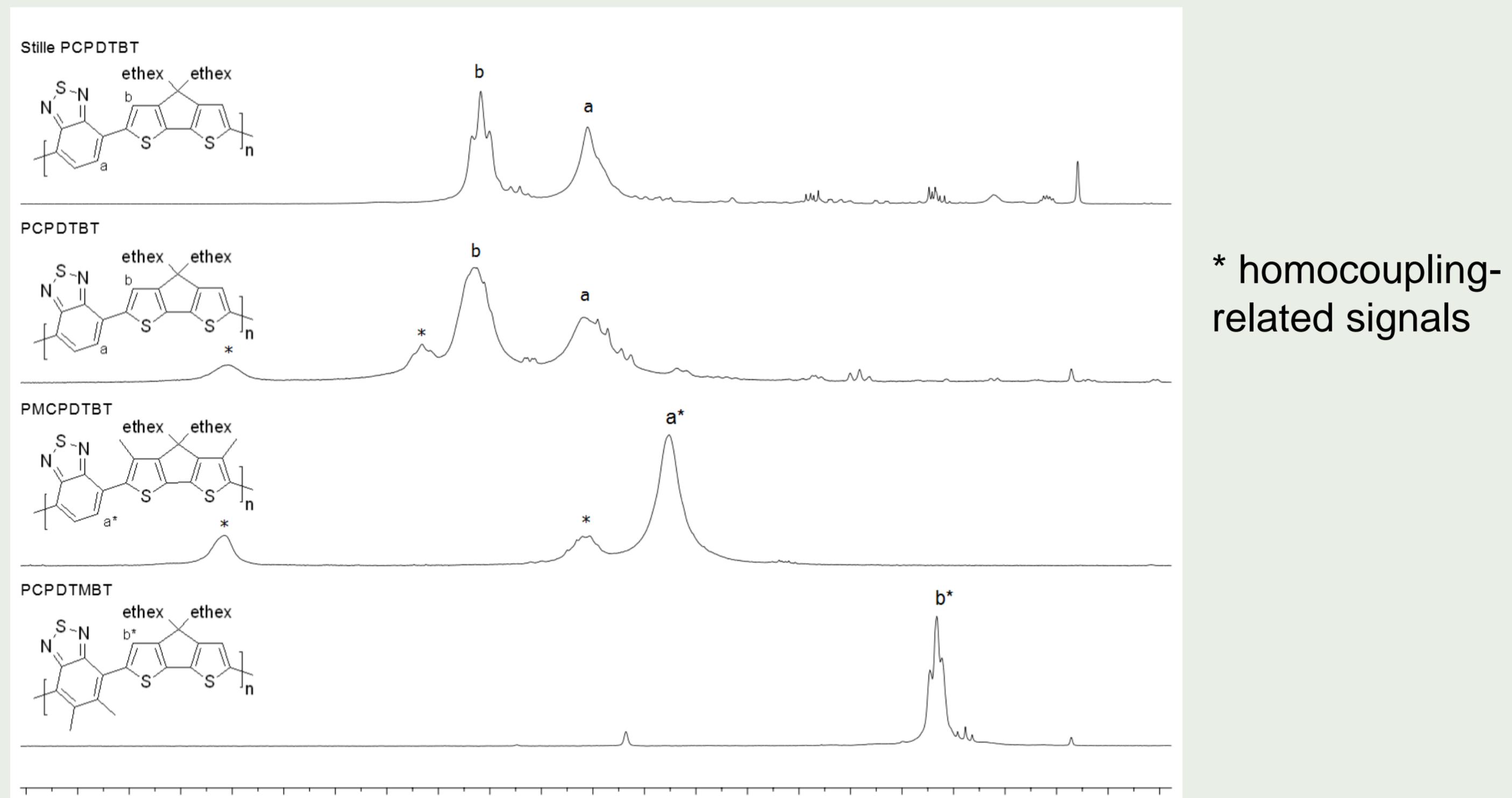
Direct (hetero)arylation polycondensation (DArP) has attracted increasing interest in the synthesis of conjugated polymers as a simple and environmentally friendly method without the use of organometallic reagents or boronic acids/esters. Nevertheless, the mechanism is not fully understood yet. Earlier work by us^[1] and others mentioned the occurrence of misconceptions during DArP. Now, we investigated a series of PCPDTBT-type copolymers and found that homocoupling is the dominating side reaction, which can be suppressed by a careful choice of the reaction parameters.^[2]

PCPDTBT-type copolymers with different degree of methylation^a:^[2]



entry	catalyst	time [h]	fraction	M _n [g/mol]	M _w /M _n	yield [%]
PCPDTBT	Pd(OAc) ₂	24	chloroform	40300	3.48	70
PMCPDTBT	Pd(OAc) ₂	24	DCM	43600	2.52	67
PCPDTMBT	PdCl ₂ (MeCN) ₂	24	hexane	27000	2.33	12 ^d
PMCPDTMBT	PdCl ₂ (MeCN) ₂	5	hexane	10200	1.79	49
			DCM	18700	2.16	20

^a Reactions were carried out at 110 °C using K₂CO₃ (2.5 equiv.) and KOAc (1.0 equiv.) as base in DMAc (10 ml). ^b Estimated by gel permeation chromatography (GPC) with polystyrene calibration. ^c The yield is based on the amounts of high molecular weight fractions after solvent extraction. ^d a major portion of the polymer was insoluble



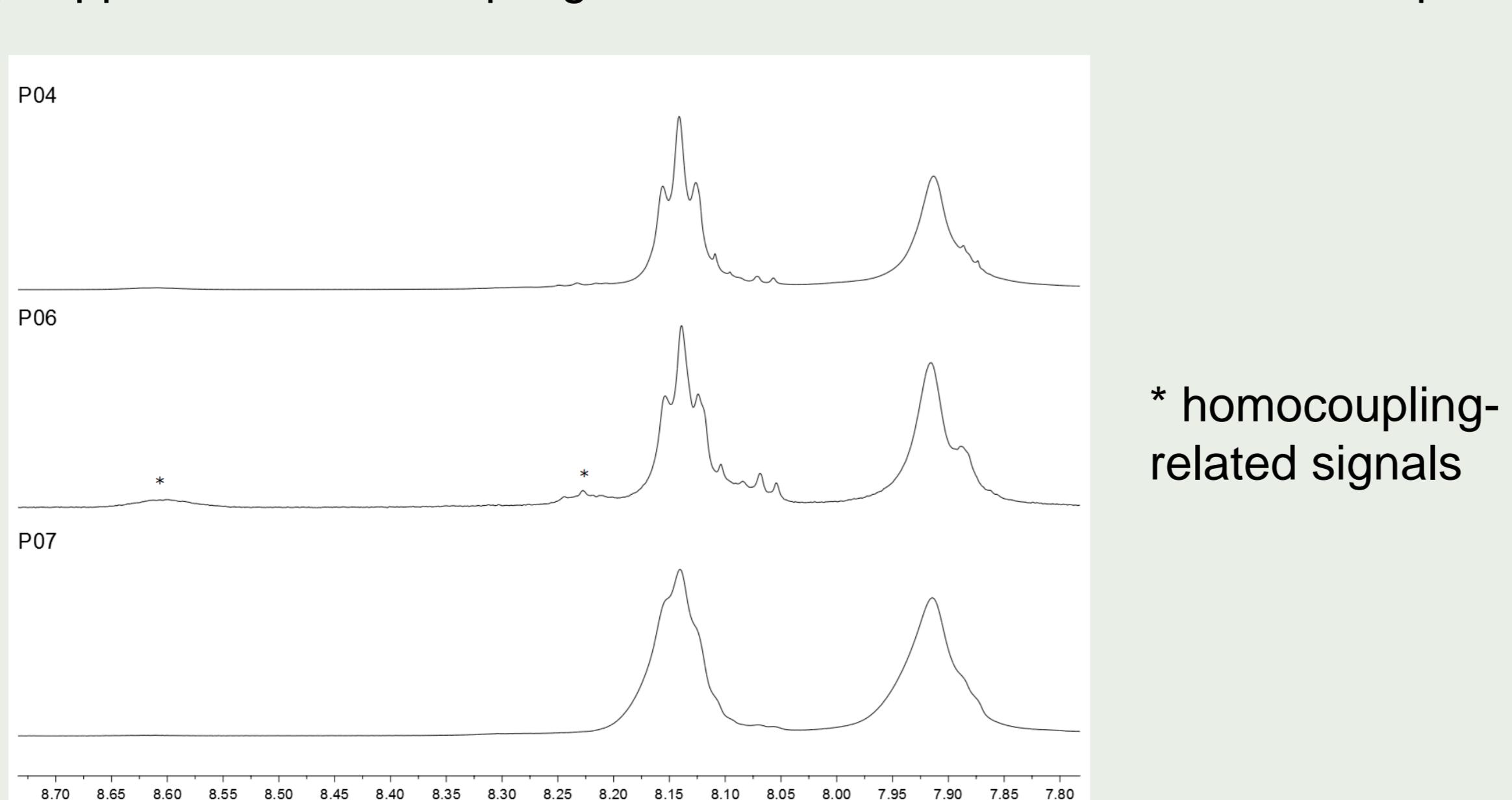
The aromatic regions of ¹H NMR spectra of the PCPDTBT-type copolymers depicted above show that homocoupling of BT units can occur during direct arylation polycondensation (8.61 and 8.23 ppm for PCPDTBT, and 8.62 and 7.91 ppm for PMCPDTBT, respectively).

Optimization of reaction conditions for PCPDTBT synthesis:^[2]

entry	catalyst	base	ligand	solvent	time [h]	fraction	M _n [g/mol]	M _w /M _n	yield [%]
P01	Pd(OAc) ₂	K ₂ CO ₃		DMAc	24	chloroform	40300	3.48	70
P02	Pd(OAc) ₂	K ₂ CO ₃	L1	DMAc	72	DCM	24600	3.91	80
P03	Pd(OAc) ₂	Cs ₂ CO ₃		DMAc	24	DCM	13700	1.55	47
						chloroform	21600	1.67	13
P04	Herrmann-Beller	K ₂ CO ₃		DMAc	72	chloroform	38200	2.10	40
P05	PdCl ₂ (MeCN) ₂	K ₂ CO ₃		DMAc	48	DCM	47300	4.56	27
						chloroform	148600	3.49	19
P06	PdCl ₂ (MeCN) ₂	K ₂ CO ₃	L2	DMAc	72	DCM	16900	1.35	18
P07	PdCl ₂ (MeCN) ₂	K ₂ CO ₃	L2	THF	72	DCM	9300	1.31	27
						chloroform	16000	1.34	20

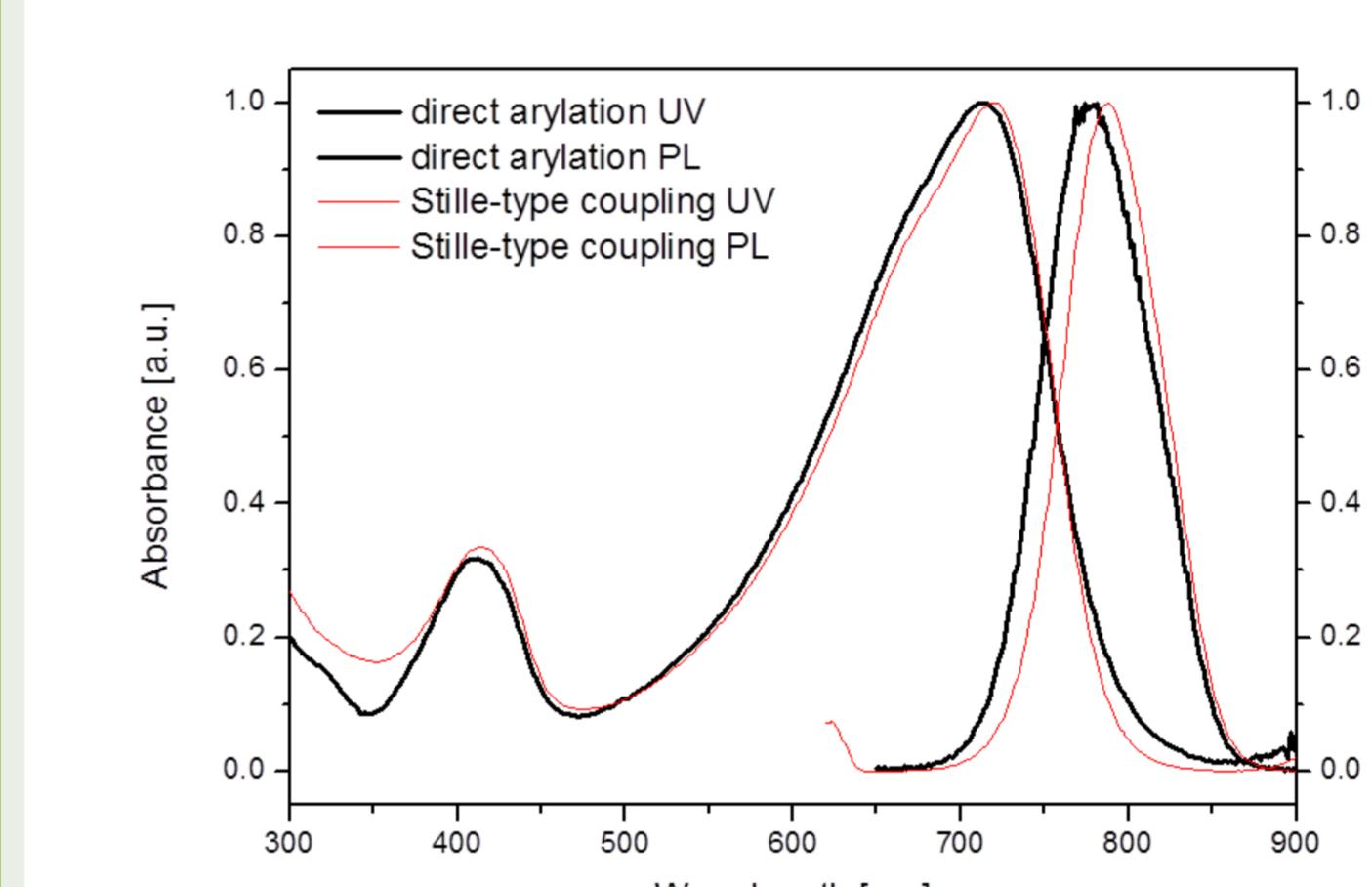
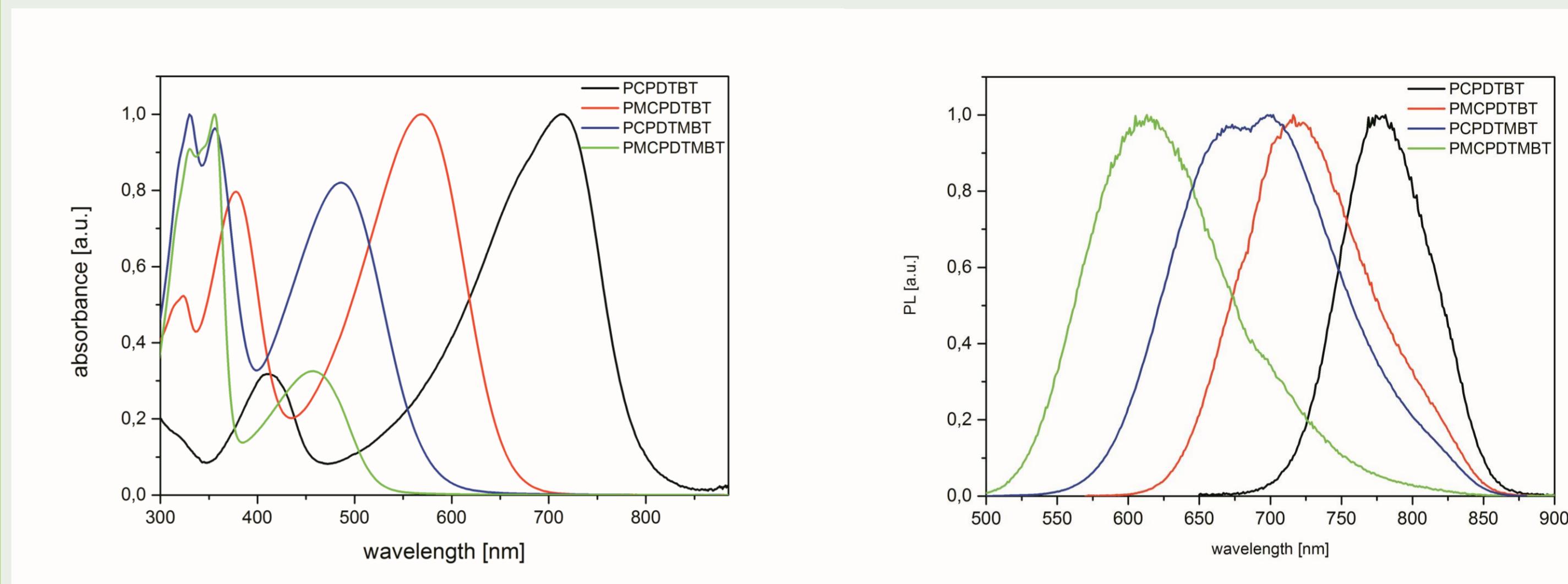
L1 = Tricyclohexylphosphonium tetrafluoroborate, L2 = tris(2-methoxyphenyl)phosphine

Use of the Herrmann-Beller catalyst in DMAc (entry P04) or PdCl₂(MeCN)₂ in presence of potassium acetate and tris(2-methoxyphenyl)phosphine as coordinating phosphine ligand in THF (entry P07) suppresses homocoupling of BT units as shown in the ¹H NMR spectra below.



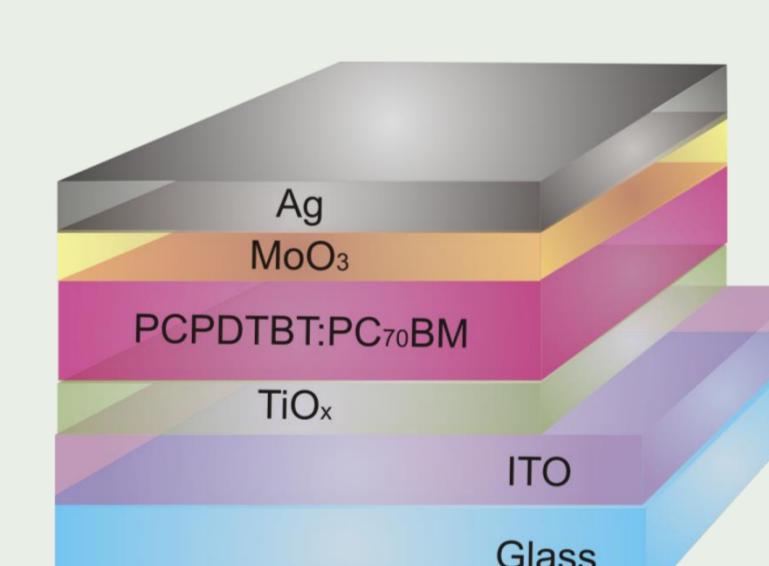
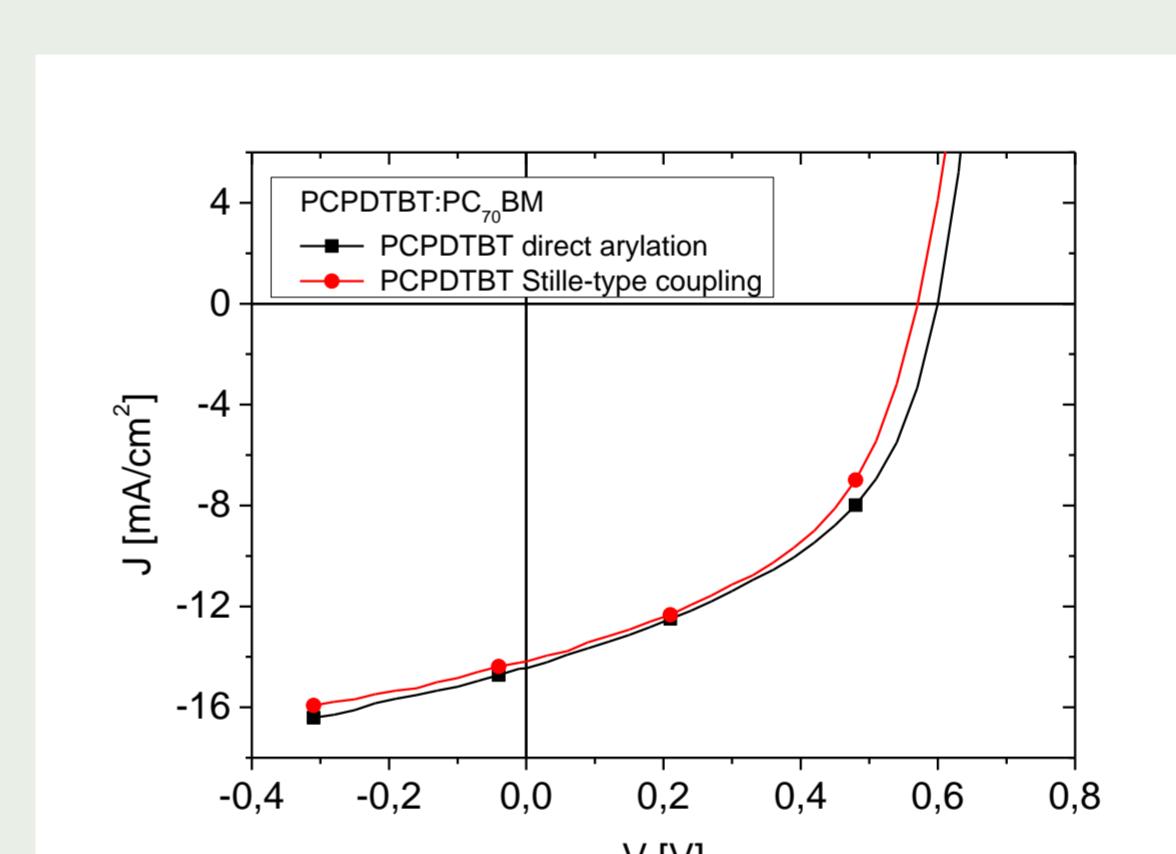
Properties of PCPDTBT-type copolymers

With an increasing degree of methylation the UV/Vis and PL bands of our PCPDTBT-type copolymers show a blue-shift which is caused by mutual distortion of the aromatic building blocks.



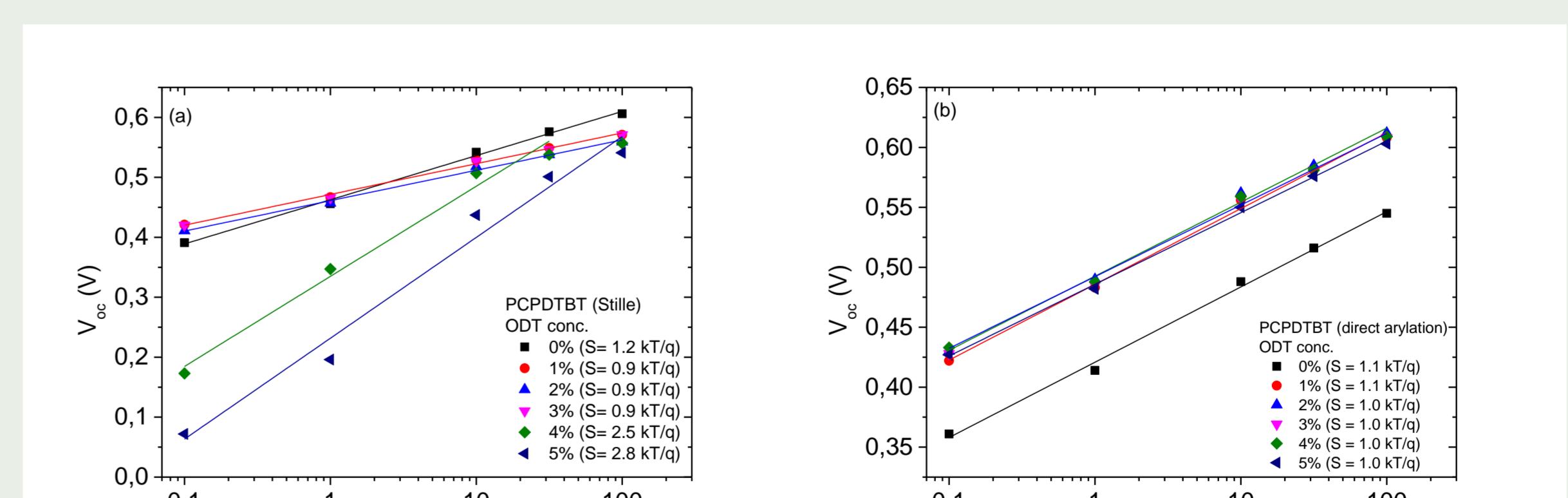
A PCPDTBT batch synthesized by DArP that contains homocoupled BT units (entry P01) shows just a very weak blue shift of the UV/vis and PL bands in comparison to a PCPDTBT batch synthesized by Stille-type coupling.

Device characteristics of inverted bulk heterojunction organic solar cells (OSCs):^[3]



I/V-characteristics of inverted OSCs with PCPDTBT as donor and PC₇₀BM as acceptor (solvent: chlorobenzene, processing additive: octane-1,8-dithiol).

PCPDTBT:PC ₇₀ BM – inverted OSCs	PCE [%]	V _{oc} [%]	J _{sc} [mA/cm ²]	FF [%]
PCPDTBT - conventional	3.8	0.57	14.2	46.6
PCPDTBT - direct arylation	4.0	0.60	14.5	45.9



V_{oc} vs. logarithmic illumination ln(I) intensity of inverted OSCs based on PCPDTBT/PC₇₀BM prepared by (a) Stille-type coupling and (b) by DAP. The slope S of V_{oc} vs. ln(I) is close to kT/q indicating the absence of trap assisted recombination due to impurities or defects.^[4-6] Only for increased amounts of processing additive ODT OSCs based on Stille-type PCPDTBT show an increased S value.

Conclusion:

Direct arylation polycondensation (DArP) is a powerful and effective tool for the synthesis of PCPDTBT derivatives. It combines low catalyst loadings with environmentally friendly reaction conditions. Homocoupling as side reaction can be suppressed by the right choice of the reaction conditions. In bulk heterojunction-type organic solar cells the use of PCPDTBT batches made in DArP or Stille-type coupling causes very similar device performances.